# Seeing Lithium Atoms by Sub-Ångstrom High-Resolution Electron Microscopy

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Sub-Ångstrom TEM of materials is growing as techniques of focal-series reconstruction and electron holography become available to retrieve the electron wave at the specimen exit-surface. SÅTEM will become widespread once correction of spherical aberration is common. Nanotechology requires "eyes" to "see" what we build, and HRTEM at sub-Ångstrom resolution fills this essential role.

Although the heavier (metal) atoms are now routinely imaged in TEM specimens at resolutions from 2Å to 1.5Å, better resolution (near 1Å) is required to "see" lighter atoms such as oxygen, nitrogen and carbon. Following the successful imaging of carbon atoms in diamond [1] and nitrogen atoms in GaN [2], we have investigated the imaging of even lighter atoms in the presence of heavy ones by using the LBNL One-Ångstrom Microscope (OÅM) to examine specimens of $LiCoO_2$. The OÅM is a combination of a modified CM300 [1] with software for reconstruction of the specimen exit-surface electron wave (ESW) from focal-series of images [3,4]. It is capable of 0.78Å resolution [5].

$LiCoO_2$ (Fig.1) is one of the most commonly used positive electrode materials in rechargeable lithium batteries for portable electronic applications such as laptop computers. The mechanism of energy storage is based on lithium insertion and extraction from the $CoO_2$ host structure. Atomic arrangements of lithium ions have a profound effect on the electrochemical performance. The objective of this study was to attempt to atomically resolve the lithium ions. The unit cell of $LiCoO_2$ is hexagonal with a = b = 2.816Å and c = 14.05Å. In [110] projection the two-dimensional cell is 2.44Å by 14.05Å with columns of cobalt, oxygen, and lithium atoms arranged in rows (Fig.2).

ESW simulations of $LiCoO_2$ do not change significantly with resolution in the range 0.8Å to 1.0Å. Atom positions have peaks that grow with increasing thickness as more atoms are added to the columns. Initially, peaks are proportional to atom mass (Fig.3), but when phases exceed $\pi$ white peaks turn black – at 8 cells (23Å) for Co columns (Fig. 3) and 22 cells (62Å) for oxygen columns (Fig.4). Although the lithium column does not reach $\pi$ by 40 cells (113Å), its peak broadens with thickness (Figs.3, 4). For 15 to 19 cells, oxygen has a sharp peak, Co is fuzzy and Li is weak (Fig.3).

A series of 20 images was obtained on the OÅM over a defocus range from -2600Å to -2144Å. The ESW-phase image was reconstructed and shows all three types of atoms with sharp bright oxygen, fuzzy Co and weak Li (Fig.5a). The inset simulation for 0.9Å resolution and 48Å thickness confirms the identification of the atom columns (Fig.5b). Simulations from a model structure with Li atoms removed confirm that the weak phase peaks at the Li positions are due to the presence of Li (Fig.6).

The match between experiment and simulation is not exact. The specimen is slightly tilted, smearing the oxygen peaks along the diagonal and displacing the lithium peaks from their central positions between the O-Co-O units. In addition, electron beam damage may have caused atom displacement or specimen buckling. Since specimen tilt reduces dynamical electron scattering, the physical thickness of our tilted specimen is probably greater than the 48Å indicated by the matching simulation [6]. Nevertheless, we have extended the range of detectable light atoms to lithium by imaging columns of cobalt, oxygen, and lithium atoms in a transition metal oxide structure commonly used as positive electrodes in lithium rechargeable batteries [7].

1. M.A. O'Keefe et al., *Ultramicroscopy* **89** (2001) 4: 215-241.
2. C. Kisielowski et al., *Ultramicroscopy* **89** (2001) 4: 243-263.
3. W.M.J. Coene, A. Thust, M. Op de Beeck & D. Van Dyck, *Ultramicroscopy* **64** (1996) 109-135.
4. A. Thust, W.M.J. Coene, M. Op de Beeck & D. Van Dyck, *Ultramicroscopy* **64** (1996) 211-230.
5. M.A. O'Keefe, E.C. Nelson, Y.C. Wang & A. Thust, *Philosophical Magazine B* **81** (2001) 11: 1861-1878.
6. M.A. O'Keefe & V. Radmilovic, *51st Ann. Proc. MSA, Cincinnati, Ohio* (1993) 980-981.
7. Work supported by the Director, Office of Science, through the Office of Basic Energy Sciences, Material Sciences Division, of the U.S. Department of Energy, under contract No. DE-AC03-76SF00098 and National Science Foundation International Research Fellow Award INT-0000429.

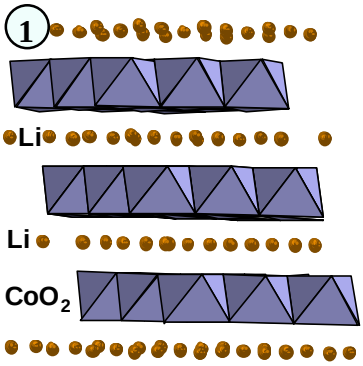



**Fig. 1** (left). $LiCoO_2$ structure consists of $CoO_2$ octahedra with chains of Li atoms lying horizontally in the spaces between them.

**Fig. 2** (below left). Projection of $LiCoO_2$ unit cell in [110] direction has horizontal rows of Li, Co, and O atoms (arrowed). In projection, cell is 2.44Å by 14.05Å, with a repeat distance in the [110] direction of 2.816Å.

**Fig. 3** (below). Simulated ESW-phase images at 0.9Å resolution for specimen thickness from 4 to 18 cells (11Å to 51Å) show white peaks at the positions of the atom columns.

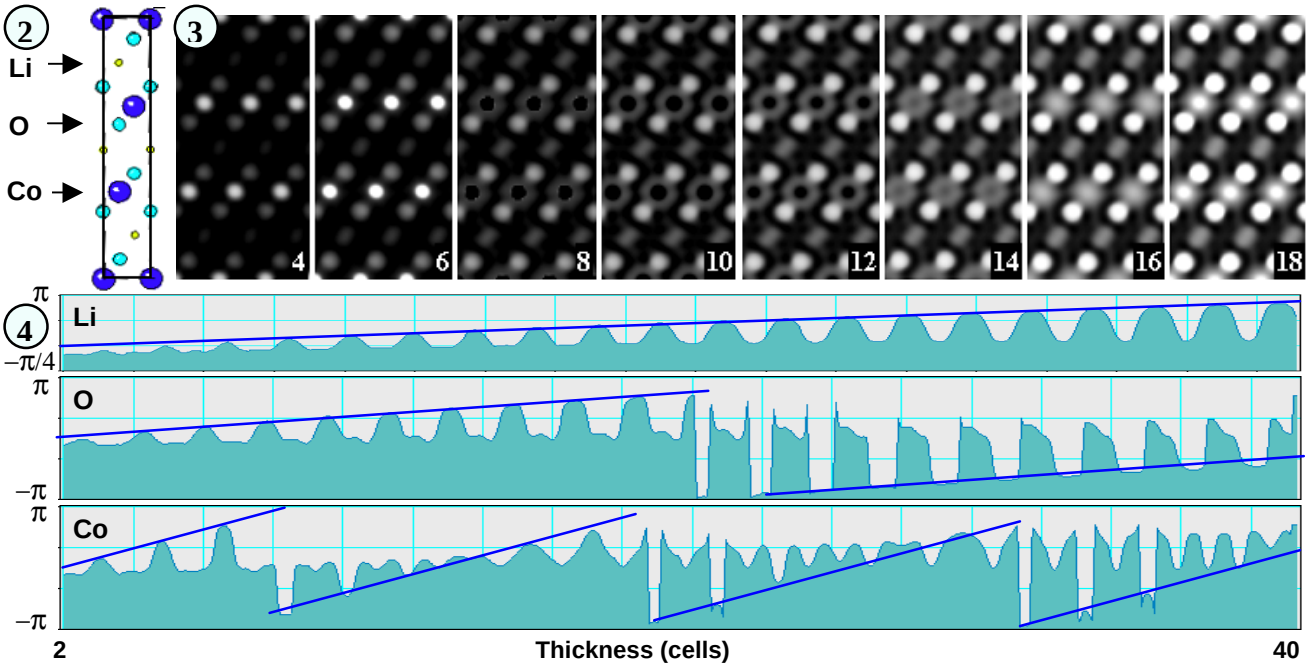
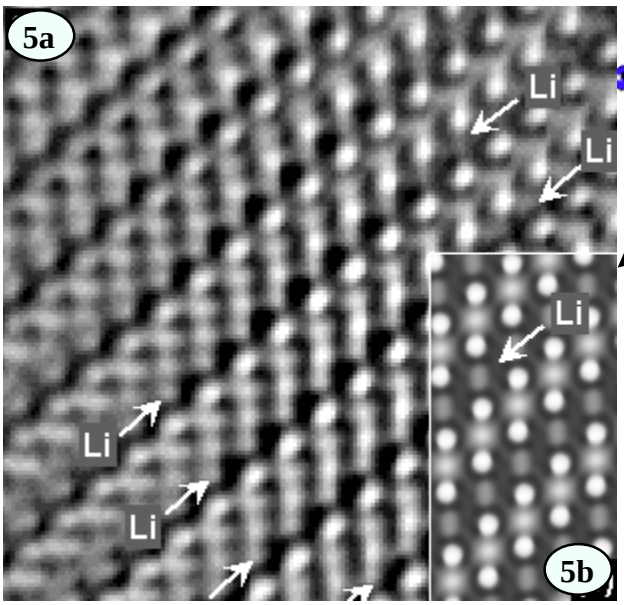



**Fig. 4**. Profiles of ESW-phase at Li, O, and Co positions for thickness from 2 to 40 cells (6Å to 113Å) show that phase peak is approximately proportional to specimen thickness and slope is greater for heavier atoms.



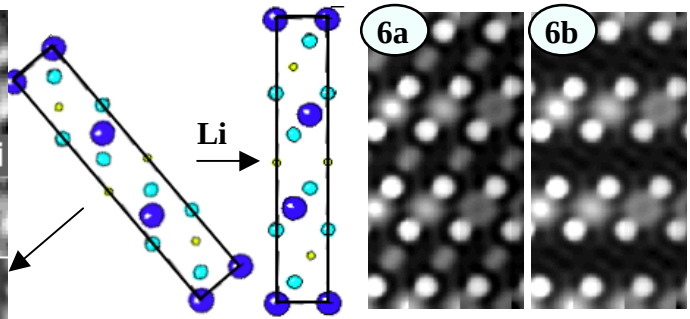




**Fig. 6**. ESW-phase simulations from models (a) with Li and (b) without Li.

**Fig. 5.** (a) ESW-phase reconstruction from 20 experimental images for defocus from -2600Å to -2144Å shows rows of atoms (top right to bottom left). Oxygen peak is strong, Co is fuzzy, and Li (arrowed) is weak. (b) Inset ESW-phase simulation at a thickness of 17 cells (48Å) confirms the identities of atom peaks.